Kinetics and mechanism of the reaction between maleic anhydride and fatty acid esters and the structure of the products

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Alkenyl succinic anhydrides (ASA) were obtained by reaction between maleic anhydride and high-oleic sunflower oil (HOSO) esters. A kinetics study of the maleinization of alkyl esters indicated that the maleinization reaction was second order overall and first order with respect to the individual reactants, and the activation energy was 77.2 ± 3.3 kJ/mol in the investigated temperature range (185–225 °C). These results showed that the *cis* configuration and the central position of the double bond in HOSO esters facilitate the maleinization of the latter. On the contrary, the length of the linear ester moiety had no influence on the course of the maleinization reaction. Moreover, new evidence demonstrates that there are two different reaction mechanisms: ene-reaction and addition in allylic position with a 2 : 1 ratio, respectively. This ratio was constant throughout the reaction, thus indicating that these mechanisms are independent.

Keywords: Activation energy / Alkenyl succinic anhydride / Ene-reaction / Maleinization / Reaction order

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1 Introduction

Alkenyl succinic anhydrides (ASA) are widely used in the paper industry as paper sizing agents [1, 2]. Other common applications include: wood preservation agents [3], additives for lubricants [4], and monomers for the fabrication of thermosets as the anhydride moiety can react with diamines, diols, polyols or epoxy resins to yield unsaturated polyester-like resins [5]. ASA are obtained by reaction between maleic anhydride and an alkene, which is usually a petrochemical olefin, but vegetable oil derivatives can also be used.

On the one hand, industrial olefins for ASA production are straight or slightly branched 16 to 18 carbon chains. Isomerization of α-olefins is performed first, to avoid terminal double bonds. The unsaturation (mainly *trans*) is therefore situated at any internal position in the chain and shows a stronger electronic density than α-olefins.

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On the other hand, the vegetable oil derivatives used for ASA synthesis are mostly unsaturated fatty acid esters. The main difference to olefins is not only the ester moiety, but also the double bond which is always located in the same position and exclusively in the *cis* configuration.

The maleinization of alkenes is a complex reaction and, currently, two different mechanisms are known: the ene-reaction and the addition in allylic position. In this regard, the literature concerning the reaction between maleic anhydride and unsaturated molecules can be divided into three periods. Firstly, the studies of the reaction mechanism during the 1940's and up to the early 1950's employed fatty acids or fatty acid esters as alkenes. The mechanism of the maleinization was debated (ene-reaction *versus* cyclization or Diels-Alder-type reaction) and, finally, the ene reaction was retained during this period [6–8]. Secondly, the strong development of petrol resources in the early 1950's favored the production of ASA from straight or branched olefins or even from polyolefins [9, 10]. Since then and up to the 1990's, the studies aimed only at limiting secondary products by adding reaction catalysts (phenothiazine, aluminum acetylacetonate) [11], polymerization inhibitors (hydroquinone, dimethylsulfoxide) [11], or dispersing solvents (toluene) [12], but no discussion about the mechanism was proposed. Thirdly, with the rising

interest in renewable resources observed since the early 1990's, new ASA have been synthesized again from vegetable oils and their derivatives. During this period, Holmberg and Johansson [13] proposed, by using an oxidative cleavage technique, two different reaction mechanisms for the maleinization of ethyl oleate leading to different isomers in the reaction products. In the first path, the anhydride is grafted on either of the two allylic positions of the alkene, leading to reaction products with the unsaturation retained at the 9–10 position (Fig. 1, reaction A). In the second path, the ene-reaction occurs on either of the two ethylenic carbons, yielding products in which the double bond of the alkene has undergone an allylic shift (Fig. 1, reaction B). According to these authors, for the oleic esters, four isomers, only *trans*-configured, are possible.

After the 1990's, no additional study has been published concerning the mechanism of the maleinization. Even if Holmberg and Johansson demonstrated that there were two routes, only the "ene-reaction" term continues to be incorrectly used, instead of the general "maleinization" term. One aim of the present work is to confirm (or to disprove) the mechanism proposed by these authors and the structure of the resulting molecules by using advanced NMR, which is a direct analysis technique and constitutes an alternative to the indirect oxidative cleavage method. Another goal of the present work is to investigate the reaction kinetics of maleinization with vegetable alkenes, which have regained industrial importance. The results will be compared with the literature that gives information about the petrochemical unsaturated molecules [11, 14, 15]. High-oleic sunflower (HOSO) alkyl esters were chosen as starting materials. Reaction order, reaction rate constant and activation energy were thus investigated.

2 Materials and methods

2.1. Materials

Alcohols (ethanol, propanol, butanol, pentanol), oleic acid alkyl esters (methyl, ethyl, propyl, butyl, pentyl), maleic anhydride as well as dibutyltin oxide and $CDCl_3$ were all 99% pure and purchased from Sigma-Aldrich (France). All reagents were used without further purification.

Different alkyl esters of HOSO were used as raw materials for the synthesis of different ASA. The HOSO methyl esters [$C_{18:1}$ (86.2%), $C_{18:2}$ (6.0%), $C_{16:0}$ (3.1%), $C_{18:0}$ (2.6%)] used in this work were provided by Novance (France). HOSO ethyl, propyl, butyl and pentyl esters were prepared from HOSO methyl esters by transesterification as described below.

Ethanol, propanol, butanol or pentanol (62.1–118.8 g), HOSO methyl esters (400 g) and dibutyltin oxide (6.7 g) were placed in a 500-mL three-neck reactor equipped with a nitrogen input, a mechanical stirrer and a reflux condenser. The

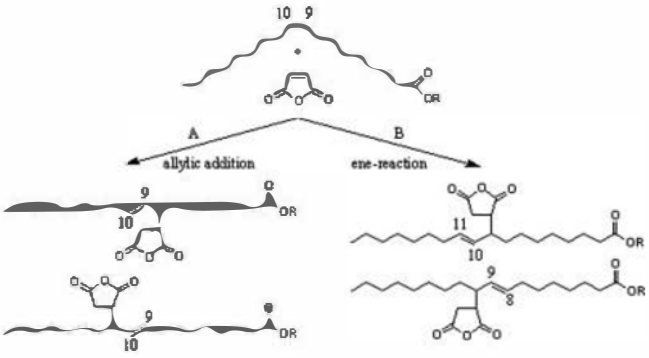

Figure 1. Maleinization of alkyl oleates proceeding by two different routes.

temperature was gently raised to the boiling point of the alcohol. The reaction was conducted for several hours, until complete consumption of the methyl oleate (monitored by HPLC). Then, the HOSO alkyl esters were distilled from the reaction medium between 160 and 170 °C under 1 mbar and immediately used for the maleinization.

HPLC analyses confirmed that the maximum amount of residual methyl ester reaction was 1.1%. The fatty acid profile for all the alkyl esters was essentially the same as that of the HOSO methyl esters. The alkyl esters were therefore obtained in high yield by transesterification (>98%).

2.2 Synthesis and purification of ASA

2.2.1 Syntheses for the kinetics study

The reagent mass values are presented for the particular case of HOSO methyl esters with a molar ratio equal to 1. All the other syntheses followed the same protocol; only the quantities varied. HOSO methyl esters (80 g) and maleic anhydride (23.2 g) were introduced into a 250-mL three-neck reactor equipped with a magnetic stirrer and a condenser heated at 60 °C. The latter was necessary to allow maleic anhydride (m.p. 53 °C) to reflux. Prior to the reaction, oxygen was removed by applying a vacuum (40 mbar) for 30 minutes. The medium was heated at constant temperature (185–225 °C according to the experiment) for 8 h under static nitrogen atmosphere. The molar ratio was calculated by assuming that one mole of alkyl oleate consumes one mole of maleic anhydride whereas one mole of alkyl linoleate consumes two moles. Sampling (0.2 mL) was carried out every hour and was analyzed by HPLC.

2.2.2 Syntheses and purification for the mechanistic study

The synthesis protocol was the same as above except that, at the end of the reaction, the medium was vacuum-distilled. The unreacted maleic anhydride was distilled at 70 °C under

1 mbar. Unreacted HOSO alkyl esters were distilled at 160 and 190 °C under 1 mbar. ASA were finally distilled in only one fraction between 240 and 250 °C under the same pressure. The purity and the structure of the distilled ASA were assessed by HPLC, infrared and NMR spectroscopy.

2.2.3 Preparation of ASA standards

ASA standards for analytical purposes were synthesized in the same manner as presented above (Section 2.2.2) by using oleic acid alkyl esters (98% purity) as raw materials, then vacuum-distilled. HPLC analyses were carried out to confirm the absence of residual alkyl esters and maleic anhydride. The purity of all the ASA standards was higher than 99.9%. Mass spectrometry and NMR spectroscopy analyses confirmed the desired structure.

2.3 Analytical methods

2.3.1 HPLC

The HPLC system was composed of a Dionex P680 pump and a Shodex refractometer detector RI 101 at 35 °C. A silica-grafted C_{18} Omnispher column of 25 cm and a diameter of 4.6 mm (Chromspher; Varian) was operated at 35 °C with a 1.5 mL/min ($P = 70$ bar) acetonitrile flow in the mobile phase. Alkyl oleates (98%; Sigma-Aldrich, France) and distilled ASA standards (see Section 2.2.3) were used as external standards to determine the composition of the reaction media.

2.3.2 Infrared spectroscopy

A drop of liquid was put between KBr windows to perform infrared analyses. Spectra were recorded in a JASCO FTIR 460 Plus apparatus in the 400–4000 cm^{-1} region with a 4 cm^{-1} resolution.

2.3.3 NMR spectroscopy

^{1}H and ^{13}C NMR spectra were recorded in a Bruker Avance apparatus at 500 MHz. The samples were analyzed in $CDCl_3$. J-modulated spin-echo (Jmod) and HSQC ($^{1}J_{H\text{-}C}$) techniques were employed. The coupling constants were calculated by the standard Bruker software.

3 Results and discussion

3.1 Study of the maleinization mechanism

The methodology used recognized that the ASA synthesis followed two paths, as described by Holmberg and Johansson [13]. Then, ^{1}H and ^{13}C NMR analyses were performed on pure molecules to assess: (i) the *cis* or *trans* configuration of the ASA and (ii) the relative concentrations of the carbon atoms labeled 8, 9, 10, and 11 in Fig. 1. These concentrations were used to determine the relative proportions of molecules following paths A and B. NMR was chosen as an analytical tool because it was the only method allowing the direct and quantitative measurement of the four positional isomers and it also provided their configuration.

The five pure (*i.e.* without residual reagents) ASA were named: methyl oleate succinic anhydride (ASAMe), ethyl oleate succinic anhydride (ASAEt), propyl oleate succinic anhydride (ASAPr), butyl oleate succinic anhydride (ASABu) and pentyl oleate succinic anhydride (ASAPe). They were all clear yellow oily liquids (Gardner color from 5 to 7).

The FTIR spectra of oleic ASA presented the characteristic bands of the expected groups. The major infrared peaks arising from anhydride carbonyl stretching were located at 1785 and 1863 cm^{-1}. They also showed a stretch vibration band typical for five-membered cyclic anhydrides (*i.e.* succinic anhydride) at 917 cm^{-1}. The carbonyl stretch band of the alkyl ester appeared at 1732 cm^{-1}. The band at 970 cm^{-1} indicated the presence of *trans* double bonds.

^{1}H NMR spectra of the samples showed the expected characteristic peaks. The example of ASAMe showed a peak at 5.5 ppm (m,2H) belonging to the –CH of the unsaturation. The peaks at 4.0 ppm (s,3H) and 1.5 ppm (m,2H) belonged respectively to the $–CH_3$ and the $–CH_2$ in the ester part. The peaks between 3.1 and 2.6 ppm (m,3H) were assigned to –CH belonging to the succinic link and to the anhydride moiety. The peaks at 2.2 ppm (t,2H) and at 1.5 ppm (m,2H) were respectively identified as the $–CH_2$ in the α and β positions to the ester group and part of the unsaturated chain. The peak at 1.9 ppm (d,2H) belonged to the $–CH_2$ in the α position to the unsaturation. Finally, the peak at 0.80 ppm (t,3H) can be assigned to the terminal $–CH_3$ moiety of the alkyl chain. These spectra provided the confirmation of the chemical nature (grafted anhydride on fatty chain) of the distilled samples. Moreover, no peak was detected for residual reagents (maleic anhydride, alkyl esters), side-products or disubstituted ASA (reaction between maleic anhydride and linoleic esters). This observation strengthened the HPLC analysis that showed only the presence of oleic ($C_{18:1}$) ASA molecules (> 98%).

The configuration of the isomers was determined by ^{13}C NMR. ASAMe, for instance, showed: δ 14.20 (CH_3), 22.75 (CH_2), 24.95 (CH_2), 27.20 (CH_2), 28.70 (CH_2), 29.02 (CH_2), 29.09 (CH_2), 29.20 (CH_2), 29.33 (CH_2), 29.42 (CH_2), 29.56 (CH_2), 30.33 (CH_2-CO-O-CO), 31.93 (CH_2), 32.55 (CH_2), 34.11 (CH_2), 42.76 (CH), 45.71 (CH-CO), 51.52 (CH_3-O), 126.17 (CH=), 126.37 (CH=), 127.16 (CH=), 127.42 (CH=), 136.21 (CH=), 136.56 (CH=), 136.61 (CH=), 136.89 (CH=), 170.69 (COO-CH_3), 173.22 (C=O), 174.29 (C=O). A magnification of the 120–140 ppm region corresponding to the double bond carbons is presented in Fig. 2.

HSQC (1JH-C) analysis provided the coupling constants (Fig. 3). The values for the hydrogen chemical couplings (15–16 Hz) confirmed the presence of only *trans* compounds,

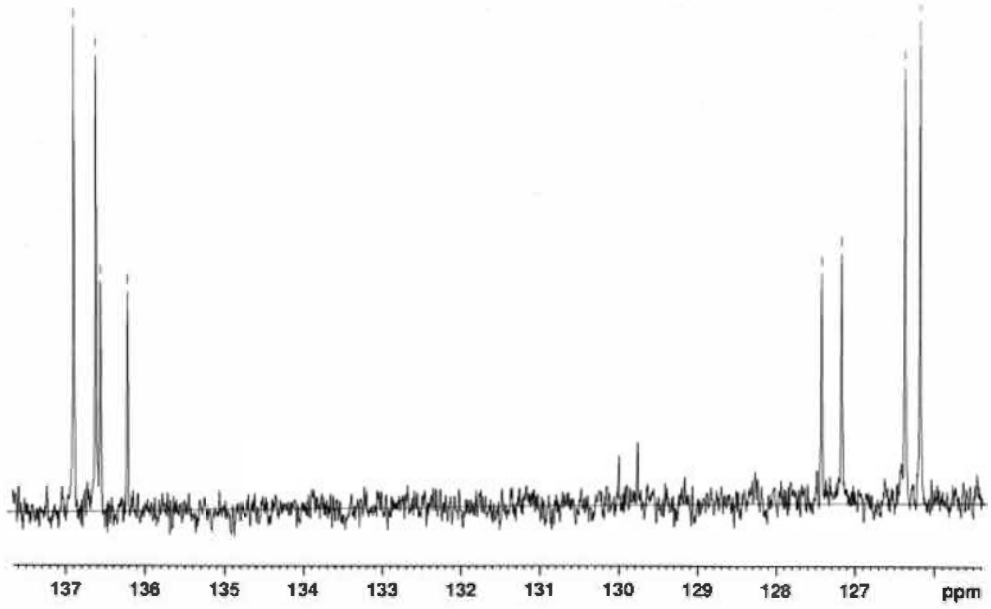

Figure 2. ^{13}C NMR spectrum of ASAMe.

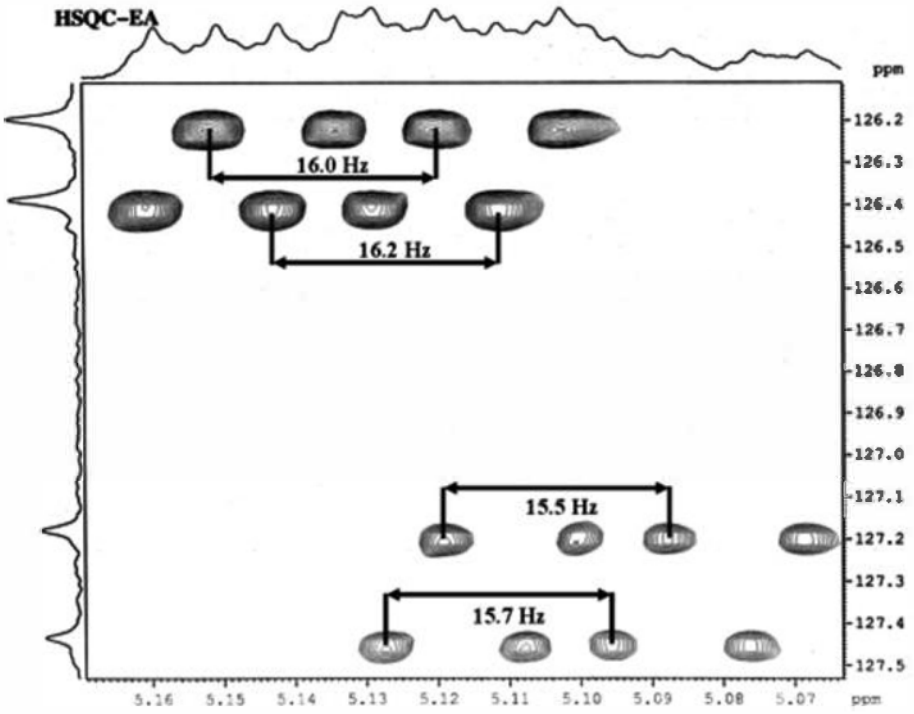

Figure 3. HSQC NMR spectrum of ASAMe.

which had already been observed [16, 17]. The *cis* configurations possess smaller coupling constants (6–14 Hz).

^{13}C NMR Jmod allowed the identification of all the kinds of carbon atoms in the molecule. According to their environment, this technique showed that in the 120–140 ppm region only olefinic carbons were present. The absence of quaternary (C) carbon atoms in this zone demonstrates that maleic anhydride did not graft to a carbon belonging to the double bond.

Moreover, the resonance zone of the ethylenic carbon atoms in the ^{13}C NMR spectrum showed a number of eight signals (Fig. 2). This means that four different compounds

were present. Paths A and B from Fig. 1 are therefore possible. The isomer distribution is related to the signal strength from which the relative isomer composition can be estimated. It is clearly seen that the concentration of products from path B is approximately two times greater than that of the products from path A. This implies that the relative isomer composition is given by either the ratio b/a = 2 or a/b = 2. It can also be observed that the most abundant compounds bear the most and the least deshielded ethylenic carbon atoms (around 137 and 126 ppm, respectively). The environment of every ethylenic carbon (highlighted in Fig. 1) is practically equivalent with regard to the anhydride cyclic group. Therefore, deshielding will depend only on the distance of the double bond to the ester moiety. Only the molecules obtained through path B are the ones that contain the C8 and C11 ethylenic carbons. On the contrary, path A yields molecules bearing only C9 and C10 ethylenic carbons. It can therefore be concluded that it is the ratio b/a that is equal to 2. The ene-reaction is thus twofold preponderant compared to the addition in allylic position. These results are in agreement with those obtained by Holmberg and Johansson [13] by oxidative cleavage of the remaining olefinic bond of the adducts and the subsequent analysis of the products (indirect method). Moreover, this ratio remained constant during the course of the reaction (sampling and analyses performed every hour). This fact demonstrates that these reactions are parallel and independent.

3.2 Kinetics study

The linoleate esters (6%) contained in the HOSO esters were rapidly transformed into linoleic ASA (disappearance of the HPLC peak) within the first hour of reaction. The kinetics study was therefore carried out on the most abundant molecule: oleic alkyl esters (86.2%).

3.2.1 Yield and conversion rate

The yield of ASA (Fig. 4) was calculated as the ratio between the number of moles of ASA determined by HPLC analysis and the number of moles of alkyl oleate initially introduced into the reactor. The conversion rate (Fig. 5) was calculated as the ratio between the number of moles of reacted alkyl oleate (evaluated by the difference after HPLC analysis) and the initial number of moles of alkyl oleate. Preliminary work concerning the synthesis of ASA from sunflower oleic acid methyl esters showed optimal reaction conditions (molar ratio MA/AE = 1.3) [18, 19]. They were used in this work.

Both parameters increase with temperature. Nevertheless, at a given temperature and ratio MA/AE, the conversion rate was higher than the yield. It can be concluded that a part of the methyl oleate and maleic anhydride was not transformed into ASA but consumed by side-reactions to form oligomers, as described previously [18, 19].

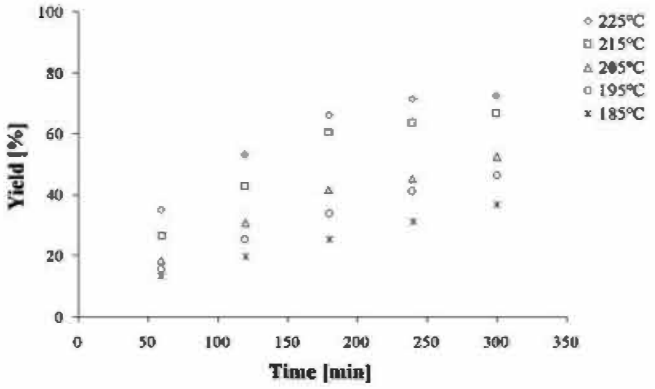

Figure 4. Effect of reaction temperature on the yield of ASAMe.

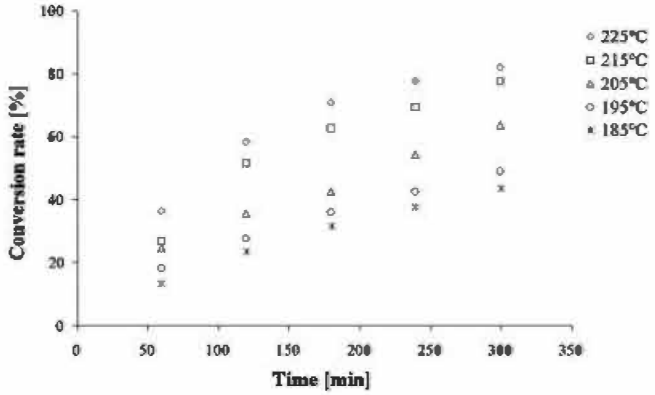

Figure 5. Effect of reaction temperature on the conversion rate of methyl oleate.

3.2.2 Reaction order and reaction rate constant (*k*)

The kinetics of the ene-reaction between maleic anhydride and various alkenes has been reported [14, 15] to be second order overall and first order with respect to the individual reactants. We assumed this dependence of the reaction rate on each reactant and worked with equimolar concentrations for the reagents. The linear plots of reciprocal concentration *versus* time for methyl oleate (Fig. 6) confirmed a first-order dependence of the reaction rate on methyl oleate and maleic anhydride concentrations. From the slopes of these plots, the *k* values were evaluated for different reaction temperatures. They increased with temperature, from 0.005 L/mol/min at 185 °C to 0.017 L/mol/min at 225 °C. In every case, the reaction order obtained for vegetables ASA with central *cis* configuration was the same as that of the petrochemical unsaturated molecules mainly *trans* reported in the literature [15].

3.2.3 Activation energy

From the Arrhenius-type plot (Fig. 7) the activation energy was calculated: E_a = 77.2 ± 3.3 kJ/mol. It is interesting to

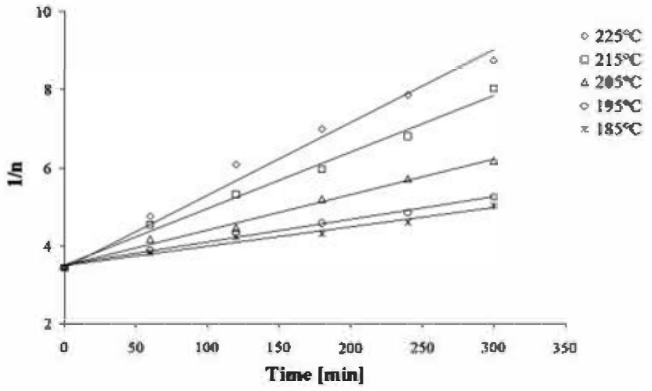

Figure 6. Second-order plot of the maleinization for different temperatures. Molar ratio = 1.

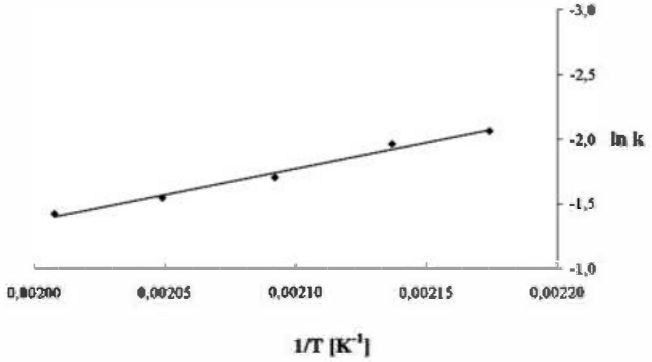

Figure 7. Arrhenius plot for the maleinization of methyl oleate.

compare this value with the results obtained by Benn and Dwyer [15], who investigated the reaction between maleic anhydride and dec-1-ene or dec-5-ene. They noticed that the lower electronic density of the dec-1-ene double bond resulted in a higher activation energy for the maleinization. This is the reason why α-olefins are isomerized to obtain scrambled β, γ, δ ... olefins to increase the electronic density of the double bond and therefore increase their reactivity towards the enophile [2].

In this study, the electronic density of the double bond of methyl oleate is ostensibly the same as that of isomerized olefins. The only difference between them is the double bond configuration. The activation energy for the maleinization of isomerized olefins reported in the literature [11] is 83.7 kJ/mol. The difference in activation energy is small but significant. It indicates clearly that *cis*-configurated molecules react more readily than *trans*-configurated ones.

3.2.4 Influence of the ester moiety

Yield and conversion rate results for ASAEt, ASAPr, ASABu, and ASAPe were similar to those obtained in the preliminary study on ASAMe. Conversion rate (Fig. 8) and

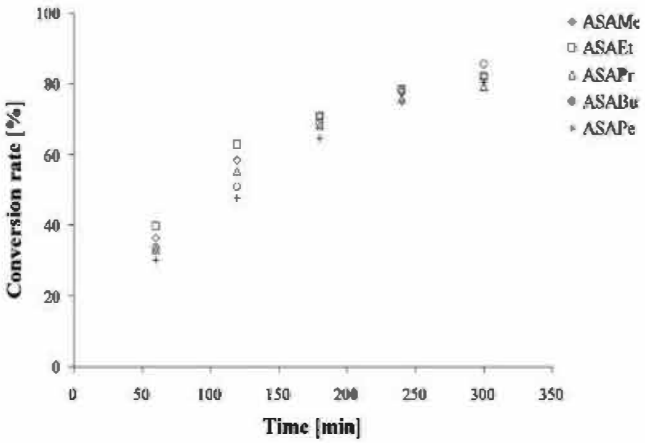

Figure 8. Effect of the ester moiety on the conversion rate of alkyl oleate.

yield (not shown) plots followed the same trend. There is no significant influence of the length of the alkyl chains on these parameters.

It was also observed that the order and the rate constant for the maleinization did not vary with the nature of the ester moiety. This group is far away from the reaction site, and the electronic density of the double bond remains essentially the same. In a comparative study that employed a molar ratio of MA/AE = 1.3, the calculation of the rate constant is based on the following equation:

$$\text{rate} = k_{\text{apparent}}\,[\text{alkyl oleate}]^{\alpha}$$

Even though k_{apparent} is different from k, for comparative purposes, the influence of the ester moiety could be investigated. At 225 °C, k_{apparent} was in the range of 0.036 ± 0.002 L/mol/min for all the ASA. Again, there was no significant influence of the ester alkyl chain on the maleinization reaction. It can be presumed that the activation energy for each reaction, from methyl to pentyl oleates, will be approximately the same. Therefore, the *trans* C_{16}–C_{18} olefins would require more energy for reaction than the *cis* vegetable molecules studied here, which bear 19 and up to 23 carbon atoms.

4 Conclusions

The results of this work can be summarized as follows:

(1) The maleinization of the alkyl esters proceeds by two competing mechanisms: ene-reaction (enophile + ene-compound) and addition in the allylic position with a 2 : 1 ratio, respectively. The reaction between alkenes and maleic anhydride should not be simply called "ene-reaction".

(2) There is always a total conversion of the *cis* double bond to a *trans* configuration.

(3) Maleinization of molecules bearing a center *cis* double bond follows a second-order reaction kinetics with an activation energy of 77.2 ± 3.3 kJ/mol, which is slightly lower than

that of the scrambled *trans* olefins, even if the latter bear less carbon atoms.

(4) The length of the linear ester moiety has no influence on the development of the maleinization reaction.

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Conflict of interest statement

The authors have declared no conflict of interest.

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